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Chlorine-free delignification of chemical paper pulp - by successive stages of treatment with oxygen, removal of metal ions, treatment with hydrogen peroxide and treatment with a peroxy acid.
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Process for delignification of a chemical paper pulp using reagents contg. no reactive chlorine, comprises a sequence of successive treatment stages Q'Q'P'A in which 0 = treatment with oxygen Q = decontaminating the pulp by removal of metal ions with a sequestering agent; P=treatment with alkaline H2O2 and A = treatment with a peroxyacid.

USE/ADVANTAGE - Esp. for delignification and bleaching of kraft pulps and sulphite pulps. The process gives efficient delignification and bleaching of the pulp with minimum degradation of the cellulose and uses reagents which are free from reactive C1. High quality pulps with a good degree of whiteness are obtd.

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Title Terms: CHLORINE; FREE; DELIGNIFY; CHEMICAL; PAPER; PULP; SUCCESSION; STAGE; TREAT; OXYGEN; REMOVE; METAL; ION; TREAT; HYDROGEN; PEROXIDE; TREAT; PEROXY; ACID
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In the translated portions that follow, the point where the translation begins and the point where it ends are indicated in square brackets.

[page 4, line 14] According to the invention, the second treatment stage is a stage in which the pulp is decontaminated from its metal ions (Q-stage). According to the invention, the Q-stage consists in treating the pulp with at least one sequestering agent [page 4, line 17]... (The document specifies some phosphates, acids and their salts and mentions that the acid DTPA has given excellent results.)

[page 4, line 28] The Q-stage can also, as a variant, consist in a treatment by an acid without a sequestrant. [page 4, line 29]

[page 5, line 4] When a sequestrant is present, a small amount of acid can be added in the Q-stage.

The amount of acid which should be added depends on the type of wood and the amount of the metallic contaminants which it contains. Usually such an amount of acid is applied that the pH of the pulp will be higher than about 5 and preferably about 5.5. The amount of acid is, however, often adjusted so that the pH does not exceed 7 and preferably not 6.5. When no sequestrant is present in the Q-stage, the pH is controlled so as to render the milieu markedly more acid, i.e. lower than 5 and preferably about 4.5. However, in order not to damage the pulp, the pH is usually not lowered to a value below 2.0 and preferably below 2.5.

When present, the amount of sequestrant applied in the Q-stage is usually lower than 1.5 g per 100 g of dry pulp. In most cases the amount is lower than 1.0 g of sequestrant per 100 g of dry pulp.

The Q-stage is usually carried out at a pressure near the atmospheric and a temperature sufficient for guaranteeing an effective consumption of the acid and/or the sequestrant and at the same time not too high so as not to damage the pulp and not causing burdensome energy costs for the heating applied in the stage. In practise, a temperature of at least 40°C and preferably at least 50°C is suitable. Advantageously the temperature should, however, not exceed 100°C and preferably not 90°C. The best results are obtained at about 60°C.

The duration of the Q-stage should be sufficient for guaranteeing a complete reaction. Apart from the fact that longer durations do not have any effect on the degree of delignification of the pulp and on its strength qualities, it is not advisable to prolong the duration of the reaction beyond what is necessary for completing the reaction in order to limit the investment cost and the energy cost for the heating of the pulp. In practice, the duration of the pretreatment can vary within a wide range, for instance from 15 minutes to about several hours, depending on the type of equipment used and the acid chosen as well as on the temperature and the pressure. Durations of at least 10 minutes and preferably at least 15 minutes are usually sufficient. However, it is important that the duration of the pretreatment does not exceed 60 minutes and preferably not 40 minutes. A duration of about 30 minutes has given excellent results.

The Q-stage is usually carried out at a consistency of the pulp of at least 2 % dry substance and, preferably, at least 2,5 % dry substance. In most cases the consistency does not exceed 15 % and preferably not 10 %. A consistency of 3 % dry substance has given excellent results.

According to the invention, the third treatment stage is a stage with alkaline hydrogen peroxide (P-stage). [page 6, line 17]

[page 6, line 34] The temperature of the P-stage should be regulated so that it stays at least at 50°C and preferably at 70°C. It must not exceed 100°C and preferably not 95°C. A temperature of 90°C has given excellent results.

The duration of the P-stage should be sufficient for bringing about a bleaching reaction which is as complete as possible. It must, however, not exceed this reaction time too much as this may cause a retrogradation of the brightness of the pulp. In practice it is set at a value of at least 60 minutes and, preferably, at least 90 minutes. In most cases it should not exceed 600 and preferably not 500 minutes. A combination of a temperature of about 90°C and a duration of about 120 minutes has given good results.

The consistency of the P-stage is usually chosen to be lower than or equal to 40 w.p. dry substance and preferably to 30 w.p. dry substance. It will in most cases not be lower than 5 % and preferably not lower than 8 %. A consistency of 10 % has given good results.

An interesting variant of the method according to the invention consists in introducing gaseous oxygen into the P-stage mixed with the hydrogen peroxide (Po-stage or Op-stage).

According to the invention the fourth stage of the treatment sequence is a stage with peroxyacid (A-stage). [page 7, line 22]

[page 10, line 16] The A-stage of treatment with peroxyacid according to the invention can be performed in a wide range of temperatures. Usually the treatment with peroxyacid is carried out at a temperature of at least 40°C and preferably at least 60°C. The temperature does, however, usually not exceed 100°C and preferably not 95°C. A temperature of 90°C has led to

good results.

Usually the treatment with organic peroxyacid is effected at atmospheric pressure. The duration of the treatment d pends on the temperature and the quality of the wood which has been used for the pulp, as well as the efficiency of the cook and the preceding stages. Durations between about 60 minutes and about 500 minutes are suitable. A duration of 120 minutes has given good results.

The pH of the A-stage of treatment with peroxyacid can be an acid pH as well as an alkaline pH. A moderately acid pH is however preferred. In practice it is preferred to set the initial pH at a value of at least 3.5. An initial pH of 5 is usually not exceeded. An initial pH of 4 has led to good results.

The consistency of the pulp of the A-stage of treatment with peroxyacid is usually chosen to be lower than or equal to 40 w.p. dry substance and preferably to 30 w.p. dry substance. It will in most cases not be lower than 5 % and, preferably, not lower than 8 %. A consistency of 10 % has given good results.

It can be interesting as a variant to let the sequence of treatment stages according to the invention be preceded by at least a wash or a decontaminating pretreatment stage by means of an aqueous acid solution and/or a solution of a metal ion sequestrant (Q-stage). This wash or stage aims at extracting from the pulp contaminants in the form of metal ions which are harmful to the progress of the bleaching and/or delignification processes. All inorganic or organic acids used in aqueous solutions, alone or in a mixture, are suitable. Strong inorganic acids such as sulphuric acid or hydrochloric acid are well suited.

Advantageously the wash or the decontaminating pretreatment should be carried out in the presence of a metal ion sequestering agent. The organic acids of the class of aminopolycarboxylic and aminonophosphonic acids and their alkaline metal salts as well as the mixtures of these acids or their salts with the strong inorganic acids mentioned above are particularly well suited for this purpose. [page 11, line 24]

[page 11, line 35] The operating conditions for the decontaminating pretreatment are not critical. They hav to be determined in each specific case according to the type of paper pulp

and the apparatus in which the treatment is carried out. Generally speaking, the choice of the acid and the quantity applied should be suitable for establishing a milieu having a pH lower than 7, for instance between about 1 and about 6.5. Particularly advantageous pH values are those between about 3.0 and about 6. The temperature and the pressure are not critical, the ambient temperature and the atmospheric pressure are generally suitable. The duration of the pretreatment can vary within a wide range, for instance from 15 minutes to several hours, depending on the equipment used, the choice of the acid, the temperature and the pressure.

According to the invention, it is also possible to let the sequence of the treatment stages be followed with a supplementary delignification stage of alkaline extraction by means of a hydroxide or an alkaline metal or alkaline earth metal carbonate (E-stage). It is also possible to let it be followed with a hydrogen peroxide stage (P-stage). It can also be followed with an alkaline extraction stage strengthened by hydrogen peroxide (Ep-stage), by oxygen (Eo-stage), or by the two reactants oxygen and hydrogen peroxide at the same time (Eop-stage).

When the object is to obtain a paper pulp delignified and bleached to a high level of whiteness, it is also possible to, as a variant, supplement the delignification process according to the invention with one or several bleaching stages in which known reactants chosen from hydrogen peroxide, chlorine dioxide and sodium hypochlorite are applied.

The method according to the invention can be applied to delignification of chemical pulps of all types. It is well suited for delignification of kraft pulps and sulphite pulps. It is particularly well suited for treatment of kraft pulps.

The following examples are given to illustrate the invention, without limiting the scope of the invention.

Examples 1R and 2R (not according to the invention)

A sample of soft wood pulp which had been subjected to a kraft cook (initial whiteness 27.9°ISO according to ISO standard 2470 (1977), kappa number 26.7 measured according to SCAN standard C1-59 (1959) and degree of polymerization 1680 expressed in number of glucosic units and measured according to SCAN standard C15-62 (1962)) was treated in a sequence of 2 stages beginning with a stage with oxygen gas under pressure (O-stage)

followed by a stage with dietylenetriamin pentaacetic acid (DTPA) in an acid milieu (Q-stage).

The operating conditions for the two first stages which are common to the two examples 1R and 2R were as follows:

1st stage: stage with oxygen (O-stage)

pressure, kPa:		600
content of NaOH, g/100 g dry pulp	4	
content of $MgSO_4.7H_2O$, g/100 g dry pulp	0.5	
temperature, °C		120
duration, min.		60
consistency, w.p. dry substance	12	

2nd stage: stage with DTPA (Q-stage)

content of DTPA, g/100 g dry pulp	0.5	
temperature, °C		60
duration, min.		30
consistency, w.p. dry substance	3	

A treatment by means of the same amount of hydrogen peroxide applied in a single stage (example 1R) or in two successive stages (example 2R) was thereafter carried out.

3rd stage: stage with hydrogen peroxide (P-stage)

	Example 1R	Example 2R	
content of H_2O_2, g/100 g dry pulp	4	2	
content of NaOH, g/100 g dry pulp	3.2	2.2	
temperature, min.		90	90
duration, min.		120	120
consistency, w.p. dry substance	10	10	

4th stage: stage with hydrogen peroxide (P-stage)

content of H_2O_2, g/100 g dry pulp	-	2	
content of NaOH, g/100 g dry pulp	-	2.2	
temperature, min.		-	90
duration, min.		-	120
consistency, w.p. dry substance	-	10	

After the treatment, the kappa number, the degree of polymerization and the whiteness of the obtained pulp was measured.

The results are given in the table below:

Example No.	Final white-ness °ISO	Kappa number	Final DP
1R	76.5	6.3	1050
2R	77.6	5.7	990

Examples 3 and 4: (according to the invention)

Example 2R was repeated, the hydrogen peroxide in the fourth stage, however, being replaced by peroxyacetic acid (Example 3) or by monoperoxysulphuric acid (Caro's acid, Example 4). The operating conditions, i.e. the temperature, the duration and the consistency, were the same as in stages 3 and 4 of Example 2R. The initial pH of the fourth stage was 4 in both of the examples 3 and 4.

The amount of the reactants applied were the following:

	Example 3	Example 4
content of CH_3-CO_3H, g/100 g dry pulp 2.24	-	
content of H_2SO_5, g/100g dry pulp	-	3.35
content of $DTPMPNa_7$, g/100g dry pulp 1.0	-	

3 4 P - Pa

content of $MgSO_4.7H_2O$, g/100g dry pulp - 0.5

wherein $DTMPNa_7$ symbolizes the heptasodic salt of dietylenetriaminepenta(methylenephosphonic) acid.

The contents of 2,24 % of CH_3-CO_3H and 3.35 % of H_2SO_5 represent a quantity of active oxygen equivalent to 1 % of hydrogen peroxide, i.e. half of what was introduced into the fourth stage in example 2R.

The Caro's acid used in example 4 was a aqueous solution containing 28.3 w.p. monoperoxysulphuric acid, 1.1 w.p. hydrogen peroxide and 57.8 w.p. sulphuric acid.

The results obtained were as follows:

Example No.	Type of peracid	Final pH	Final white-ness °ISO	Final kappa number	final DP
3	CH3CO3H	3.5	75.8	3.4	1090
4	H2SO5	2.5	71.0	3.4	1010

Examples 5 and 6: (according to the invention)

The pulp obtained in examples 3 and 4 was subjected to a fifth alkaline extraction in the presence of 1.7 % of NaOH and 1 % of hydrogen peroxide.

The following results were obtained:

Example No.	Final white-ness °ISO	Final kappa number	Final DP
5	85.1	2.1	1020
6	83.8	2.4	910

O - Q - P - Pq - EP

The total amount of the oxidizing reactants applied in the sequences of the examples 1R, 2R, 5 and 6 correspond to a same quantity of active oxygen equivalent to 4 g of hydrogen peroxide for 100 g of dry pulp. It can be seen that the sequences 5 and 6 according to the invention allow obtaining a pulp which is better delignified, has a higher whiteness than and a degree of depolymerization comparable with that of the sequences OQP and OQPP of the prior art. [page 15, line 17]